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Global Biogeochemical Cycles

RESEARCH ARTICLE

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Key Points:

- Thorium-232 supply rates produce reasonable ocean replacement times for the rare earth elements
- Iron residence time in the North Atlantic may be less than 6 years
- Thorium-232 supply rates may provide an accurate basis for the supply of many other elements for constraining biogeochemical models

Supporting Information:

- Supporting Information S1
- Data Set S1

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Replacement Times of a Spectrum of Elements in the North Atlantic Based on Thorium Supply

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Abstract The measurable supply of ²³²Th to the ocean can be used to derive the supply of other elements, which is more difficult to quantify directly. The measured inventory of an element divided by the derived supply yields a replacement time estimate, which in special circumstances is related to a residence time. As a proof of concept, Th-based supply rates imply a range in the replacement times of the rare earth elements in the North Atlantic that is consistent with the chemical reactivity of rare earth elements related to their ionic charge density. Similar estimates of replacement times for the bioactive trace elements (Fe, Mn, Zn, Cd, Cu, and Co), ranging from <5 years to >50,000 years, demonstrate the broad range of elemental reactivity in the ocean. Here we discuss how variations in source composition, fractional solubility ratios, or noncontinental sources, such as hydrothermal vents, lead to uncertainties in Th-based replacement time estimates. We show that the constraints on oceanic replacement time provided by the Th-based calculations are broadly applicable in predicting how elements are distributed in the ocean and for some elements, such as Fe, may inform us on how the carbon cycle may be impacted by trace element supply and removal.

1. Introduction

The ocean is a dynamic chemical reactor. The quantity of a particular element in the ocean is the result of a balance between the rates of its supply and removal mechanisms (Barth, 1952; Broecker, 1971). For instance, most major components of sea salt are added slowly from river inflow and removed by the occasional evaporation of isolated seas. By comparing the rate of river inflow of salt to the inventory, or total amount, of salt in the ocean, one derives a replacement time (Berner & Berner, 2012), or how long it would take this source to replace all of the ocean's salt. In a steady state system where, over some geographical or temporal average, the supply rates and removal rates are equal, replacement time is equivalent to residence time. Residence time is an often-used concept in environmental studies, and its definitions vary (e.g., Bolin & Rodhe, 1973), including how quickly the component cycles through the system or on what time scales we might expect variations in the concentration of this component. Because in general the steady state assumption is difficult to satisfy, here we emphasize the more general concept of a replacement time. In this study, we define replacement time as the time it would take to replace the inventory of an element by a defined source for a given volume of seawater. A practical limitation of this definition, given the localized nature of oceanographic observations, is that elemental inventories and sources may not be colocated. Geographical extrapolation is one way to deal with this issue. Nonetheless, examining local variations in replacement times may provide insight into the geographical distribution of either elemental inventories or sources.

The replacement times (or residence times) of trace elements are difficult to constrain for two reasons. First, especially for contamination prone elements, there had been a lack of globally distributed measurements to

define their inventories. Second, parameters used to estimate elemental fluxes, such as input rates, are challenging to measure directly, and often a small number of discrete flux measurements were extrapolated over the global ocean. This has hindered our ability to accurately model the marine cycling of these elements. A metric for defining how these models treat Fe cycling, for instance, is to produce a global ocean Fe residence time by comparing the ocean Fe inventory to total sources in the model (which are set to equal their sinks, so in this case residence time and replacement would be equivalent). However, available global ocean biogeochemistry models produce Fe residence times that range over 2 orders of magnitude, 4 to 560 years (Tagliabue et al., 2016). This highlights the present uncertainty associated with this essential bioactive trace element's biogeochemical cycle.

Here we use a technique to estimate trace element replacement times based on dissolved thorium (Th) isotope and trace element measurements from a GEOTRACES zonal section of the North Atlantic (GA03). Such temporal information is critical for understanding the ocean's role in the Earth system, in particular for understanding the distribution and cycling of the micronutrient trace elements whose availability impacts primary productivity and thus the uptake of CO₂ into the ocean (Morel & Price, 2003; Tagliabue et al., 2014). Elements with very short replacement times (decades or less) could display biogeochemical responses to changes in trace element supply or removal that are observable on human timescales (decades to centuries).

The long-lived Th isotopes are scavenged from the ocean by adsorption onto sinking particles on timescales of years to decades, much faster than their rate of radioactive decay (half-life of ²³²Th = 14.1 × 10⁹ years; half-life of ²³⁰Th = 75.6 × 10³ years). Since the source of ²³⁰Th in the ocean, decay of dissolved ²³⁴U, is well known and homogeneously distributed, we can use the oceanic distribution of ²³⁰Th to quantify a rate of Th scavenging or the inverse of the residence time with respect to scavenging (τ_{Th} in equation (1)). In the case of ²³⁰Th, its residence time with respect to scavenging is equivalent to its replacement time with respect to production via uranium decay. In support of this statement, it has been shown in models and observations that at any given water column in the ocean, scavenging removal is within 30% of production due to uranium decay (Hayes, Anderson, et al., 2015; Henderson et al., 1999).

Common Th, ²³²Th, is supplied to the ocean by continental material, such as mineral aerosol dust (referred to simply as dust in this manuscript) or seafloor sediments (Bacon & Anderson, 1982), and is assumed to be scavenged at the same rate as ²³⁰Th. By making a steady state assumption for the level of ²³²Th in the ocean, ²³²Th scavenging rates must be matched by supply of ²³²Th by the partial dissolution of continental material (Hayes et al., 2013; Hirose & Sugimura, 1987; Hsieh et al., 2011; Huh & Bacon, 1985). The ocean residence time of dissolved Th based on ²³⁰Th inventories in the upper 4 km of the GA03 section ranges from 14 to 28 years across the basin (Hayes, Anderson, et al., 2015). Given this short residence time, it is likely that the steady state assumption holds for ²³²Th throughout most of the ocean, and its replacement time due to continental material dissolution is likely equivalent to its residence time with respect to scavenging. Using these assumptions, one can derive a dissolved ²³²Th flux supplied to the ocean simply by measuring dissolved ²³⁰Th and ²³²Th inventories in the ocean (equation (1)).

Combining Th residence times with the measured dissolved ²³²Th inventories produces an estimate of dissolved ²³²Th flux, $F(^{232}Th)$, as a function of integration depth (Figure 1; equation (1); see Hayes et al., 2017 for more details). In equation (1), there is more than one way to provide consistency between units among these terms, but here we give one way with each term followed by an appropriate unit. First, ²³²Th inventories are calculated by integrating ²³²Th concentrations, resulting in a molar amount of ²³²Th per square meter. The τ_{Th} in the denominator, in years, on the right-hand side of the equation, results from taking the integrated production of ²³⁰Th by ²³⁴U decay, in this case given in units of ²³⁰Th radioactivity, Bq per square meter per year, and dividing by the integrated inventory of ²³⁰Th, also in units of radioactivity. In these units, the integrated ²³⁰Th production would be simply, $\lambda_{230}^{234}U$, where ²³⁴U concentration is also in units of Bq, the decay constant λ_{230} being about 9.17 × 10⁻⁶ year⁻¹.

$$F(^{232}Th) = \frac{\int_0^z d^{232}Th \, dz \left[\frac{mol}{m^2} \right] \times \int_0^z (\lambda_{230}^{234}U) \, dz \left[\frac{Bq}{m^2 \times year} \right]}{\int_0^z d^{230}Th \, dz \left[\frac{Bq}{m^2} \right]} = \frac{\int_0^z d^{232}Th \, dz \left[\frac{mol}{m^2} \right]}{\tau_{Th} [year]} \quad (1)$$

Next, one can derive the flux of another dissolved element, using the generic element Z, coming from the same source, $F(Z)$, using equation (2a). To do this, the input ratio of the element to Th of the dissolved

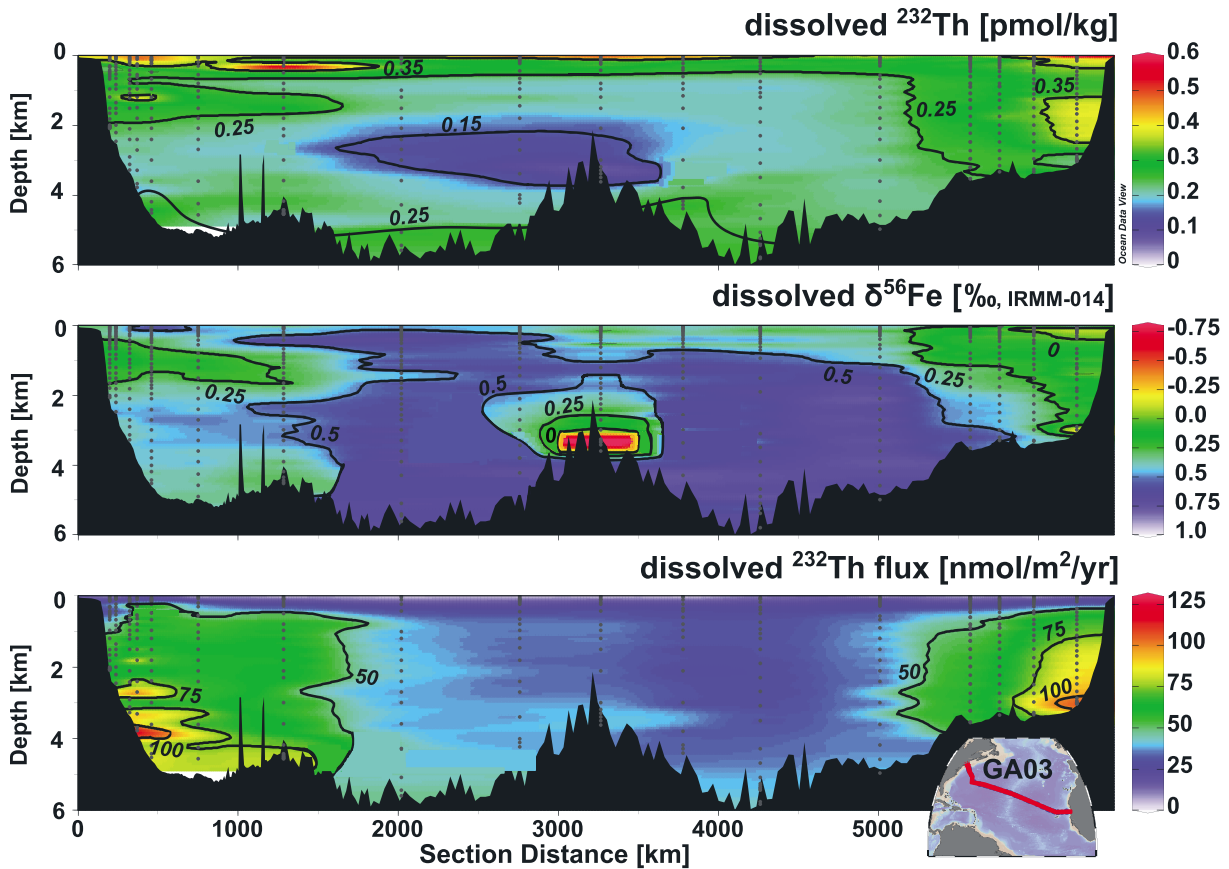


Figure 1. (top) Dissolved ^{232}Th distribution along the east-west transect of GA03. (middle) The stable isotopic composition of dissolved Fe ($\delta^{56}\text{Fe}$) (Conway & John, 2014a). Note the inverted scale on isotopic values. (bottom) The dissolved ^{232}Th flux as a function of integration depth. The inset map on the bottom right shows the GA03 cruise tracks (blue) and the section plotted here (red). IRMM = Institute for Reference Materials and Measurements.

phase associated with a particular source must be known, $(Z/\text{Th})_{\text{input}}$. Note for convenience, in equation (2) and subsequent equations, we have dropped the d to denote the dissolved phase. For the remainder of the manuscript, when referring to fluxes, replacement time or residence time of thorium or other metals, we are referring to those of the dissolved phase, unless otherwise noted.

$$F(Z) = F(^{232}\text{Th}) \times \left(\frac{Z}{\text{Th}} \right)_{\text{input}} \quad (2a)$$

$$F(Z) = F(^{232}\text{Th}) \times \left(\frac{Z}{\text{Th}} \right)_{\text{UCC}} \times \left(\frac{S_Z}{S_{\text{Th}}} \right) \quad (2b)$$

In the case of dust, this input ratio could be defined as the Z/Th ratio of leachates of collected dust samples. In the case of another potential source, such as sediment pore water, one could define the $(Z/\text{Th})_{\text{input}}$ based on the ratio of the elements measured in the dissolved phase of collected pore water samples. However, at present, the Z/Th ratios of sediment pore waters are not well known. In a more general case, an assumption could be made as to the solid phase element to Th ratio, say, for example, using the average composition of the upper continental crust (UCC). Then this solid phase ratio would be modified by biogeochemical processes during input to the oceans such as solubility, oxidation, or reduction. We subsume these processes here using the term relative fractional solubility. Fractional solubility of Z , S_Z , can also be defined by leaching experiments, in which the amount of Z that is leached from the source material is compared to the total amount of Z in the solid material used in the leach, expressed as a percentage. Relative fractional solubility of Z to Th (S_Z/S_{Th}) is therefore the ratio of the fractional solubility for the two elements. Since Th is supplied to the ocean from both dust and seafloor sediment dissolution, in this study we will use the more general

case of equation (2b). This equation uses the UCC as a source that subsumes two distinct sources (dust and seafloor sediments). If more were known about the Z/Th ratios of the benthic flux, then it could be considered separately, but in the absence of that information, we use the simplification that the composition and relative solubility of both dust and seafloor sediments are the same. Of course, many elements have important sources whose composition significantly differs from the UCC (e.g., rivers and groundwater); this is nonetheless our starting point.

The goal in deriving these elemental fluxes is to compare them with measured inventories to derive replacement times. We emphasize here that our Th-based approach will not account for some other important sources to the ocean, such as hydrothermal vents. Additionally, we are making no assessment of how our supply rates compare to the removal rates or otherwise assessing the steady state assumption. For instance, dissolved Fe can be removed from the ocean in a number of ways including scavenging, biological uptake, or inorganic precipitation (Tagliabue et al., 2017). If the sum of these removal terms were equal to our supply estimate based on ^{232}Th fluxes at steady state, then the derived replacement time would be equivalent to a residence time. Rather than assess that equivalency here, we can use the more limited replacement time concept as a way to view the relative rates of temporal cycling of a broad array of elements that have been measured in the GEOTRACES program.

We can anticipate that our replacement times will overestimate the residence time if there are sources of the elements of interest that are not accounted for by the dissolved ^{232}Th flux calculated for the North Atlantic. The sources of ^{232}Th to the North Atlantic are largely dust deposition and margin sediment dissolution. Other sources of trace elements to the North Atlantic may include hydrothermal venting, rivers, estuaries in which riverine sources can be diminished (Andersson et al., 1995; Boyle et al., 1977) or enriched (Shiller, 1997), submarine groundwater discharge, and/or water masses that advect a dissolved signal derived from processes occurring at or before their point of origin (preformed signature). At steady state all these sources will be equal to the sum of removal fluxes, again written in the form of the tracer conservation equation for the generic dissolved element, Z, in equation (3).

$$\frac{dZ}{dt} = F(\text{AD}) + F(^{232}\text{Th}) \times \left(\frac{Z}{\text{Th}} \right)_{\text{input}} + F(\text{vents}) + F(\text{rivers}) - F(\text{scav}) - F(\text{biol}) - \dots = 0 \quad (3)$$

Here $F(\text{AD})$ represents the sum of advective and diffusive circulation fluxes into or out of the box of ocean in question, $F(\text{vents})$ represents source from hydrothermal vents, $F(\text{rivers})$ represents the source from rivers, $F(\text{scav})$ represents removal by scavenging, $F(\text{biol})$ represents removal by biological uptake, and there may be many other terms in the full balance not accounted for here (represented by “...” in equation (3)).

Rearranging equation (3), we can estimate the replacement time of dissolved element Z, τ_Z , by dividing the inventory, or total amount, of dissolved Z in the ocean box in question, by the sum of its source terms (equation (4)). Inventories are calculated by integrating dissolved elemental concentrations with depth from the surface downward.

$$\tau_Z = \frac{\text{inventory of Z}}{F(\text{AD}) + F(^{232}\text{Th}) \times \left(\frac{Z}{\text{Th}} \right)_{\text{input}} + F(\text{vents}) + F(\text{rivers})} \quad (4)$$

Since the residence time of Th (decades) is much shorter than the transit time of deep ocean water masses (centuries to millennia), Th measured along GA03 likely has little preformed component. Thus, in considering water column inventories of Th, advective and/or diffusive sources can be neglected. Longer residence time elements, however, may have a substantial or even dominant preformed component. Thus, if $F(\text{AD})$ is a substantial flux for element Z, or similarly if $F(\text{vents})$ is large compared to the Th-based supply, then the replacement time we calculate by Th supply alone will overestimate the residence time. By making an area-weighted average of all the stations occupied on GA03, and assuming these stations represent the entire North Atlantic, the preformed supply of elements from North Atlantic water masses will be accounted for. Supply from outside the North Atlantic (e.g., Antarctic Bottom Water), however, would still be unaccounted for. Furthermore, if our estimate of $(Z/\text{Th})_{\text{input}}$ is higher or lower than the true value then our replacement times will underestimate or overestimate the residence time, respectively. In the case of using equation (2b) for input term, our estimate of either $(Z/\text{Th})_{\text{UCC}}$ or S_Z/S_{Th} could be biased higher or lower than the true value.

2. Methods

2.1. Data Sources

We draw upon data from previous GA03 publications of dissolved ^{230}Th (Hayes, Anderson, et al., 2015), Fe (Conway & John, 2014a; Hatta et al., 2015), Zn (Conway & John, 2014b; Roshan & Wu, 2015a), Al (Measures et al., 2015), Mn (Wu et al., 2014), Cd (Conway & John, 2015; Wu & Roshan, 2015), Cu (Jacquot & Moffett, 2015; Roshan & Wu, 2015b), and Co (Noble et al., 2017). We also use data from leaching experiments performed on aerosol material collected during the cruise (Shelley et al., 2018). Data from this transect on ^{232}Th , yttrium, and the rare earth elements (REEs) are presented here for the first time. Methods to determine dissolved ^{232}Th were reported by Hayes, Anderson, et al., 2015. Y and REE were determined by a combination of isotope dilution and external standard mass spectrometry, and detailed methods are reported by Shiller (2016a). Full section views of the Y and REE concentration sections are available at <http://egeotrac.es.org>. All GA03 data are accessible through the Biological and Chemical Oceanography Data Management Office (<http://data.bco-dmo.org/jg/dir/BCO/GEOTRACES/NorthAtlanticTransect/>) or the GEOTRACES Data Products (Mawji et al., 2015).

2.2. REE Composition and Solubility

For calculating REE replacement times, using equations (3) and (4), we define $(\text{REE}/\text{Th})_{\text{UCC}}$ based on two sources (Table 1). A published synthesis (Rudnick & Gao, 2014) defines the average values for the UCC, and a GA03 aerosol study (Shelley et al., 2015) defines end-member elemental ratios of North African dust, likely a major source of Th and REEs to this section. Both of these estimates are used in our calculations as a way of taking into account uncertainty in the source material ratios. Most of the REE/Th ratios are similar (within 30%) for the two estimates, except notably for Gd, Tb, Tm, and Lu. North African dust has a factor of 2 or more greater REE:Th ratio than the average UCC for these elements.

To define the relative fractional solubility of REEs to Th, we use results from aerosol leaching experiments of North African dust samples collected on GA03 (Shelley et al., 2018). Two types of leaches were performed on aerosol samples that were designed to represent a range in leaching intensity that continental particles experience under oceanic conditions: (1) an ultrapure (18.2 M Ω) deionized water leach (DI leach, Buck et al., 2006) and (2) a pH 2 leach consisting of 25% acetic acid and 0.02 M hydroxylamine hydrochloride with a 10-min heating step at 90–95 °C (Berger et al., 2008; HAC leach). In general, absolute fractional solubility values defined by leaching experiments have been found to be highly sensitive to experimental conditions (Morton et al., 2013). In the present study, however, only the relative fractional solubility between an element and Th is used (equation (3)), and relative fractional solubility may be less sensitive to leach method. For example, it was found that S_{Th} was an order of magnitude larger in the HAC leach compared to DI leach (Anderson et al., 2016), while REE fractional solubility relative to that of Th ($S_{\text{REE}}/S_{\text{Th}}$) differs between the two leaches by less than 30% (except for Ce, for which the HAC leach gave a 40% higher value than the DI leach; see Table 1). One previous study determined $S_{\text{REE}}/S_{\text{Th}}$ for in situ pumped lithogenic particles from the Mediterranean Sea for La, Ce, Pr, Nd, Gd, Dy, and Er, by incubating the filtered particles in seawater containing endemic bacteria under oxic conditions in the dark for several days (Arraes-Mescoff et al., 2001). This study found similar $S_{\text{REE}}/S_{\text{Th}}$ values as those reported here, averaging 3.8 ± 1.7 (avg. ± 1 standard deviation, $n = 11$) for all REEs studied, displaying no apparent trend with atomic number. Interestingly, the HAC leach values for $S_{\text{REE}}/S_{\text{Th}}$ are consistently higher than those of the DI leach (Table 1). Here to account for the uncertainty in residence time estimates induced by different leaching techniques, we have used fractional solubility ratios from both the DI leach and HAC leach in calculations.

2.3. Bioactive Trace Element Composition and Solubility

For the bioactive elements considered here (Mn, Fe, Co, Cu, Zn, and Cd) along with Al, often used as an abiotic analog for the scavenged-type trace metals, we also use both UCC and North African dust metal: Th ratios (Rudnick & Gao, 2014; Shelley et al., 2015) as a way to account for variability in source material (Table 2). These sets of ratios also are generally consistent with each other, except notably for Zn and Cd for which the North African dust metal: Th ratio is highly elevated compared to the UCC. We take this comparison with caution because it is possible that the North African dust estimates may contain Zn and/or Cd contamination from co-occurring anthropogenic emissions (Grousset et al., 1995; Shelley et al., 2015). Furthermore, as discussed further below, for some of these elements, rivers are likely the dominant source, instead of dust, to

Table 1
REE/Th Ratios of the Average Upper Continental Crust (Rudnick & Gao, 2014) and North African Dust (Shelley et al., 2015), and Deep Ocean Residence Time Estimates Made Here (See Section 3.3 and Equations (1)–(4)) Compared With Whole Ocean Residence Times Based on Deep Sea Sedimentation Removal (Li, 1991)

| REE: | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|--|----------|----------|--------|----------|----------|----------|----------|----------|----------|----------|----------|----------|---------|----------|----------|
| REE/Th UCC (mol/mol) | 5.2 | 4.9 | 9.9 | 1.1 | 4.1 | 0.69 | 0.15 | 0.56 | 0.10 | 0.53 | 0.11 | 0.30 | 0.039 | 0.25 | 0.039 |
| REE/Th North African (mol/mol) | 5.8 | 6.6 | 1.4 | 1.6 | 5.6 | 1.0 | 0.28 | 3.2 | 0.22 | 0.64 | 0.14 | 0.34 | 0.088 | 0.37 | 0.084 |
| S_{REE}/S_{Th} DI leach | 3.8 | 2.1 | 2.2 | 2.4 | 3.1 | 3.6 | 3.5 | 1.0 | 2.2 | 3.6 | 3.3 | 3.6 | 2.8 | 2.3 | 2.4 |
| S_{REE}/S_{Th} HAC leach | 4.8 | 2.7 | 3.8 | 3.4 | 4.1 | 4.5 | 3.9 | 1.4 | 2.7 | 4.5 | 3.8 | 4.0 | 2.8 | 2.5 | 2.1 |
| North Atlantic replacement time (years) | 580 ± 90 | 180 ± 30 | 15 ± 6 | 110 ± 30 | 110 ± 20 | 100 ± 20 | 100 ± 10 | 150 ± 30 | 150 ± 30 | 250 ± 40 | 310 ± 40 | 420 ± 30 | 290 ± 3 | 600 ± 30 | 440 ± 50 |
| Whole ocean residence time (Li, 1991; years) | 240 | 150 | 20 | 80 | 100 | 80 | 80 | 120 | 120 | 150 | 190 | 240 | 300 | 230 | 380 |

Note. The fractional solubility ratios (S_{REE}/S_{Th}) are derived from leaching experiments of North African dust aerosols collected on GA03 using either deionized water (DI) or a weak acetic acid-type leach (HAC). Note that only two significant figures are shown here for brevity, but at least three significant figures were used in calculations. REE = rare earth element; UCC = upper continental crust.

the North Atlantic. While the element to Th ratios in global rivers has been estimated (Gaillardet et al., 2014; Table 2), one could not use them to estimate riverine elemental supply without having a good constraint on the flux of Th from rivers alone. Additionally, element to Th ratios are likely modified in estuarine processes. Thus, we realize that making a replacement time estimate of river-supplied elements like Cd based on the sources that supply Th (dust and sediment dissolution) is apparently *mismatched*. Nonetheless, the comparison of the apparent results for these types of elements to the elements with sources more similar to Th is still useful in demonstrating the relative range of possible replacement times in the ocean.

The relative solubility will again be a major source of uncertainty for the bioactive trace metals. There are few studies that determine the relative solubility of all the elements of interest here. In particular, oceanic Th fractional solubility data are rather limited and range from about 1–29%, in published work (Anderson et al., 2016; Arraes-Mescoff et al., 2001; Hayes et al., 2017; Robinson et al., 2008; Rowland et al., 2017; Roy-Barman et al., 2002). Based on time series measurements of Th and Fe at station ALOHA (Hayes, Fitzsimmons, et al., 2015), it is likely that S_{Fe}/S_{Th} is close to 1, but this may vary regionally and episodically. However, broadly consistent with that finding, DI and HAC leaches of the North African dust aerosols from GA03 produced S_{Fe}/S_{Th} estimates of 0.4 ± 0.2 ($n = 2$) and 1.3 ± 0.3 ($n = 15$), respectively.

Mn, Al, and Co have either predominant or significant sources from atmospheric deposition to the North Atlantic basin (Measures et al., 2015; Noble et al., 2017; Wu et al., 2014). The DI leach results for S_{Mn}/S_{Th} were very variable (3841 ± 804 , $n = 2$). Thus, here, we rely more heavily on the HAC leach for S_{Mn}/S_{Th} (9.8 ± 2.4 , $n = 7$). DI and HAC leaches produced relative solubility ratios consistent with each other within uncertainty for Al ($S_{Al}/S_{Th} \sim 2$) and Co ($S_{Co}/S_{Th} \sim 6$).

As mentioned above, the sources of Cd, Cu, and Zn are likely dominated by rivers (Little et al., 2015) and not by atmospheric deposition. However, since we are defining replacement times with respect to the sources that supply Th, it is still appropriate to define the relative element to Th solubility in the sources that supply Th (namely, atmospheric deposition and sediment dissolution). The DI leach of Saharan aerosols for Zn/Th was highly uncertain ($S_{Zn}/S_{Th} = 20 \pm 19$, $n = 2$), while its HAC leach was better constrained ($S_{Zn}/S_{Th} = 6.7 \pm 3.5$, $n = 7$). Similarly, DI leaches for Cd/Th and Cu/Th were more variable but were consistent with the HAC leach within uncertainty ($S_{Cd}/S_{Th} \sim 10$ and $S_{Cu}/S_{Th} \sim 3$). Because the Th-based supply of Cd, Cu, and Zn ignores riverine input and is therefore an underestimate of the total supply of these elements, the replacement times we derive are overestimates of the residence time (equation (4)).

3. Results

3.1. ^{232}Th Distribution, Flux, and Sources

The distribution of dissolved ^{232}Th across the Woods Hole-Mauritania portion of GA03 is shown in Figure 1. Near the Mauritanian margin, dissolved ^{232}Th concentrations are elevated throughout the water column due to North African dust deposition (Anderson et al., 2016) and, to some extent, due to input from margin sediments. The dissolved ^{232}Th distribution has similarities with that of the isotopic composition of dissolved Fe ($\delta^{56}\text{Fe}$; Figure 1), indicative of a common source of these lithogenic metals. At the four easternmost stations, the dissolved Fe was characterized by lighter $\delta^{56}\text{Fe}$ values (compared to the continental crust) throughout much of the water column. Conway and John (2014a) ascribed this signal to a mixing of Fe sources of roughly 80–90% dissolution from aerosol dust (with a hypothesized isotopically heavy signature [Conway & John, 2014a; John & Adkins, 2012]) and 20–10% reducing margin sediments (with an isotopically light signature due to dissolved Fe (II) release from reducing pore waters, [Severmann et al., 2006]). Because of Th's similar distribution in concentration space to $\delta^{56}\text{Fe}$, a similar balance of sources may exist for Th. Future work may be able to independently constrain a margin sediment source of Th using the potentially quantifiable source of ^{228}Ra from the sediments (Charette et al., 2016).

Much of the deep Atlantic basin has a background dissolved ^{232}Th concentration of 0.2–0.3 pmol/kg, with a marked depletion around the Mid-Atlantic Ridge, a signal of intense Th scavenging

Table 2

Upper Continental Crustal Elemental Ratios, Relative Solubility Based on Leaching Experiments of North African Dust Aerosols From GA03, Using a Deionized Water (DI) or a Weak Acetic Acid-Type Leach (HAc), Deep Ocean (4 km) Residence Times Based on This Study (See Section 3.4 and Equations (1)–(4)), and Other Published Estimates of Deep Ocean Residence Times

| | Al | Fe | Mn | Zn | Cd | Cu | Co |
|---|-----------------------|----------------------|-----------------------|----------------------|-----------------------|-----------------------|----------------------|
| (Metal/Th) _{UCC} (mol/mol) | 33,400 | 15,500 | 312 | 22.6 | 0.0177 | 9.74 | 6.49 |
| Metal/Th North African dust (mol/mol) | 41,600 | 15,700 | 268 | 48.8 | 0.326 | 14.2 | 6.49 |
| Metal/Th rivers (mol/mol, Gaillardet et al., 2014) | 6,710 | 6,690 | 3,500 | 51.9 | 4.03 | 132 | 14.2 |
| $S_{\text{Metal}}/S_{\text{Th}}$ DI leach | 1.5 ± 0.9 (n = 12) | 0.4 ± 0.2 (n = 2) | 3841 ± 804 (n = 2) | 20 ± 19 (n = 2) | 54 ± 40 (n = 12) | 5.4 ± 3.6 (n = 12) | 14 ± 7 (n = 12) |
| $S_{\text{Metal}}/S_{\text{Th}}$ HAc leach | 2.0 ± 0.4 (n = 7) | 1.3 ± 0.3 (n = 7) | 9.8 ± 2.4 (n = 7) | 6.7 ± 3.5 (n = 7) | 10.0 ± 5.2 (n = 7) | 3.4 ± 1.1 (n = 7) | 5.9 ± 1.5 (n = 7) |
| Deep North Atlantic replacement time w.r.t Th supply (GA03; years) | 50 ± 10 | 6 ± 3 | 5 ± 1 | 1,100 ± 600 | 105,000 ± 103,000 | 5,200 ± 1,300 | 140 ± 70 |
| Other residence time estimates | | | | | | | |
| Deep Pacific residence time w.r.t. deep water scavenging (Bruland et al., 1994; years) | 45–90 | 70–140 | 20–40 | 3,000–6,000 | 22,000–45,000 | | |
| Whole ocean residence time from mass balances (Little et al., 2015, 2016, 2017; years) | | | | 8,000–11,000 | 26,000–55,000 | 2,000–3,300 | |
| Deep Atlantic residence time w.r.t. deep water scavenging (Bergquist & Boyle, 2006; years) | | 130–410 | | | | | |
| Deep Pacific (4 km) residence time w.r.t. Th supply (Hayes, Fitzsimmons, et al., 2015; years) | | 30 | | | | | |
| Whole ocean residence time from global ocean biogeochemistry models (Tagliabue et al., 2016, 2018; years) | | 4–560 | | | | | 70 |
| Whole ocean residence time (Roshan et al., 2016) | | | | 2,400–3,600 | | | |
| Deep Atlantic residence time w.r.t deep sea sedimentation (Saito & Moffett, 2002; years) | | | | | | | 40–120 |

Note. Residence time estimates are denoted by the flux with respect to (w.r.t.) which they are based. Values are limited to a maximum of three significant figures here.

(Hayes, Anderson, et al., 2015) in waters impacted by hydrothermal plumes (indicated in Figure 1 by a light excursion in dissolved $\delta^{56}\text{Fe}$ from hydrothermal iron input). In the northwestern Atlantic, Upper Labrador Seawater, seen in the section plot around 1,200-m depth from section distance 500 to 2,000 km, is characterized by elevated ^{232}Th (0.3–0.4 pmol/kg) and similarly traced by lighter (near-crustal) dissolved $\delta^{56}\text{Fe}$ compared to the background basin (Figure 1). In the case of Upper Labrador Seawater, Conway and John (2014a) ascribed the sources of dissolved Fe as 70–90% nonreductive sediment release and 30–10% aerosol dust. The seafloor sediments in the region of Labrador Seawater formation are of UCC origin, and they may face leaching-type conditions even more intense than in the water column from sediment resuspension and burrowing activity (Aller & Aller, 1986). Thick nepheloid layers were seen in this portion of the GA03 section (Lam et al., 2015). Thus, ^{232}Th may be a general tracer for continental material in the ocean, whether leached from dust or seafloor sediments.

Finally, in the upper 500 m of the section between Woods Hole and Bermuda, elevated ^{232}Th is seen in waters influenced by the Gulf Stream, consistent with previous observations off Cape Hatteras (36.1°N, 74.4°W; Guo et al., 1995). In this case of the Gulf Stream, elevated ^{232}Th concentrations appear decoupled with changes in Fe isotopic composition in contrast to the rest of the section, likely because the Gulf Stream is carrying a signal from its source regions further south.

3.2. REE Replacement Times as Proof of Concept

We begin with a focus on REEs and yttrium (in this paper we include Y when using the abbreviation REE, sometimes abbreviated as YREE) because their ocean geochemical cycles may be similar to that of Th, with supply by upper continental crustal material (including dust, riverine particles, or seafloor sediments) and

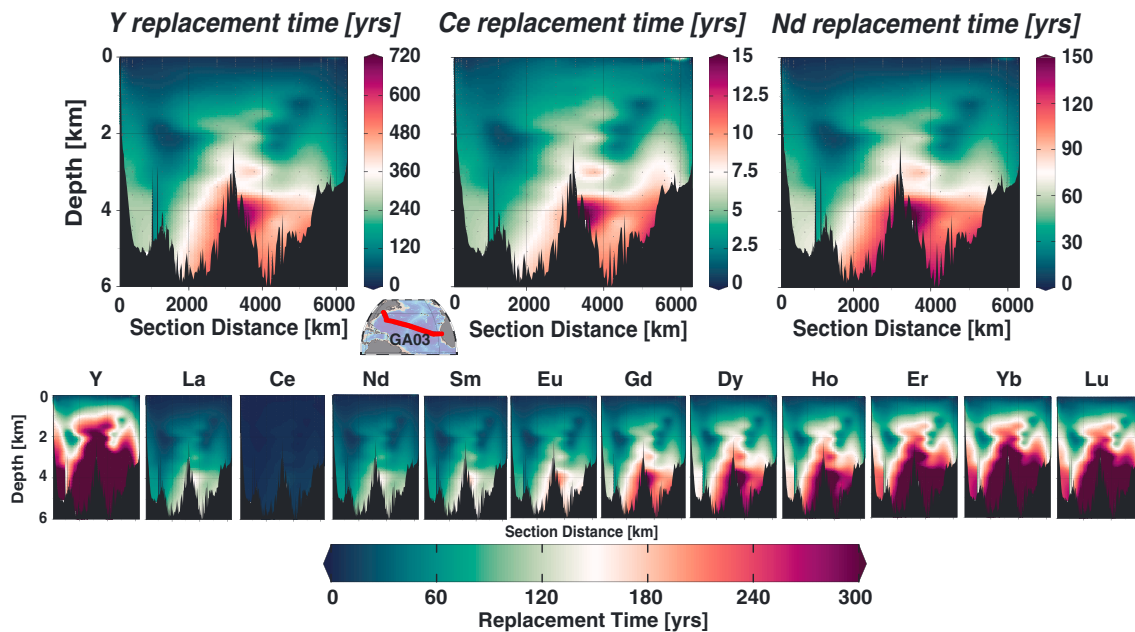


Figure 2. Replacement times of dissolved REEs (Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, and La shown here; Pr, Tb, and Tm not shown for brevity) as a function of integrated depth across the GA03 transect (small inset map). These replacement times are calculated with respect to supply based on dissolved ^{232}Th , assuming North African dust composition and HAC leach solubility ratios. The three plots in the top row are all on different colorbar scales. All plots in the bottom row use the same colorbar scale. REEs = rare earth elements; HAC = acetic acid.

removal by adsorption onto sinking particles, or scavenging (Elderfield, 1988). Additionally, REEs have generally decreasing particle reactivity with increasing atomic number. This is related to their similar valence state (3+) and decreasing ionic size with increasing atomic number. REE scavenging in seawater has been studied in detail (Byrne & Kim, 1990; Quinn et al., 2004; Schijf et al., 2015), and a gross simplification can be made that increased ionic charge density for the heavier REEs means they are more strongly complexed in seawater by carbonate ions and thus less susceptible to scavenging. Anomalous to the overall trend, seawater has low Ce/REE ratios in comparison with the UCC since Ce can exist in either the 3+ or 4+ state, the latter being much more insoluble in seawater.

The calculated replacement times of the dissolved REEs are presented in cross-section form in Figure 2 using North African dust REE/Th composition and HAC leach solubility ratios. An area-weighted average across depth horizons was also calculated to represent the basin-wide North Atlantic replacement time (see Table 1 and supporting information for averaging method and tabulated data). Replacement times generally increase with integration depth and with atomic number from roughly 5 to 500 years. The extremes are Y, with the largest of the replacement times, 580 ± 90 years for the whole North Atlantic (error representing uncertainty related to the compositional and solubility ratios), and Ce being 15 ± 5 years. We note that the derived dissolved Ce replacement time range is roughly half the residence time of dissolved Th, meaning Ce must be relatively intensely scavenged.

For most REEs the replacement time appears to increase with integration depth relatively abruptly in the deep eastern Atlantic basin below 4-km depth, compared with the western basin (Figure 2). In investigating this pattern, it is worth noting that the Mid-Atlantic Ridge hydrothermal vents are not a source of REEs to the ocean and are actually a sink from scavenging onto hydrothermal particles (Stichel et al., 2018; Zheng et al., 2016). The apparent increase in replacement time in the deep eastern basin therefore may be explained by the presence of preformed REEs transported by Antarctic Bottom Water (AABW). It has been estimated that in the deep waters of GA03 about 20% of the dissolved Nd was added from local sources (dust or sediment dissolution), the other 80% being from preformed water masses (from both the North and South Atlantic, Shiller, 2016b; Stichel et al., 2015). AABW is about 1.7 times more concentrated in dissolved Nd than lower North Atlantic Deep Water (Zheng et al., 2016). With this information and the estimate that the deep portion of GA03 is 30% AABW (Jenkins, Smithie, et al., 2015), about 25% of the deep Nd in GA03 may have originated

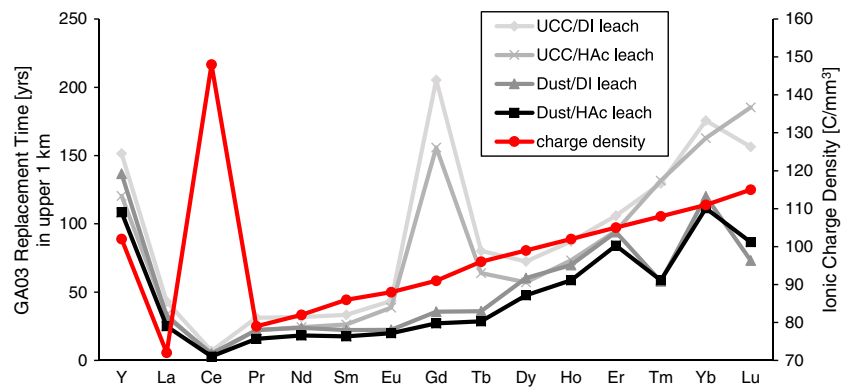


Figure 3. Average REE replacement times for the upper 1 km over the entire GA03 transect compared with ionic charge density of the same element. All elements were assumed to be trivalent cations, with the exception of Ce, for which the charge density of the tetravalent cation is shown. The grayscale curves represent the range of residence time estimates produced using different assumption for source material (upper continental crust, UCC, or north African aerosol samples, dust) and relative fractional solubility of the REE to Th (defined using either a deionized water, DI, leach or a mild acetic acid solution, HAc, leach of North African dust aerosol samples). REE = rare earth element; UCC = upper continental crust.

from outside the North Atlantic. Assuming there is no preformed ^{232}Th from AABW, the REE replacement times based on Th supply may overestimate the true North Atlantic residence time, by probably about 25%.

Nonetheless, the trend in replacement times across the spectrum of REEs is quite robust. Taking the basin-averaged replacement times at the 1-km integration depth level to reduce the effect of preformed supply (although the full water column integration results also give a similar trend), REE replacement times follow a similar trend to REE ionic charge density (Rayner-Canham & Overton, 2006, Figure 3). This is consistent with the simple prediction that at higher charge densities (i.e., heavier REEs), a greater fraction of REEs are complexed by carbonate ions, thus less susceptible to scavenging removal (with the exception of Ce). These results support the idea of inorganic complexation increasing REE residence times in the ocean, which is predicted by thermodynamic treatments (Byrne & Kim, 1990; Quinn et al., 2004; Schijf et al., 2015).

Figure 3 also shows the sensitivity of these replacement time estimates to the choice of compositional and solubility ratios. In particular, the lower Gd/Th ratio of the UCC results in a large positive anomaly in the replacement time estimate, whereas the estimates using the North African dust end-member fall in line with the atomic size trend, suggesting the North African dust end-member is a more relevant source in this area. This result suggests that anthropogenic Gd, sourced from its medical use as a contrast agent in magnetic resonance imaging, may have contaminated both North African dust and the adjacent Atlantic Ocean, as has been observed in the Mediterranean (Censi et al., 2010), the North Sea (Kulaksiz & Bau, 2007), and many other sites.

There have been prior REE ocean residence time estimates, most notably for Nd, for comparison with results reported here. Since the isotopic composition of dissolved Nd is a quasi-conservative tracer of water masses in the deep ocean (Tachikawa et al., 2017), it has been inferred that the ocean residence time of Nd must be shorter than the mixing time of the ocean ($\sim 1,000$ years). In our data set, integrating the whole North Atlantic results in a Nd replacement time of 110 ± 20 years (Table 1 and Figure 4), the uncertainty representing the variation in composition and solubility values is chosen. This estimate is shorter than the Nd residence times (200–1,000 years) calculated by comparing isotopic composition of particulate Nd with that of the surrounding seawater (Tachikawa et al., 1999). Note as well, as shown in Figure 3, that if one only considers the upper 1 km, the dissolved Nd replacement time is about 25 years, which is likely shorter than the ventilation time scale of ~ 40 years (Jenkins, Lott, et al., 2015). This suggests Nd is unlikely to trace water mass properties in the upper 1 km of the ocean, in agreement with other studies (Tachikawa et al., 2017). Additionally, a recent Eastern Equatorial Pacific study found significant changes in dissolved Nd isotopic composition through the upper 2.5 km of the water column from station reoccupations separated by only 3 years (2009 and 2012), suggesting a very rapid turnover time (Grasse et al., 2017).

Another study made basin-scale estimates of REE residence times by comparing an estimate of the global seawater inventory with removal by sinking particles (Li, 1991). While these estimates are based on much less

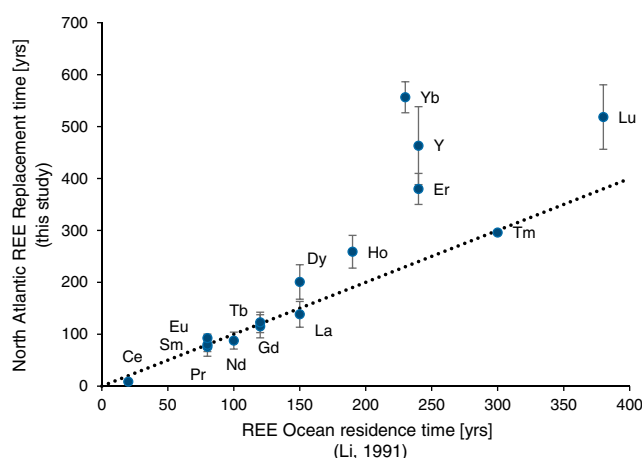


Figure 4. Rare earth element ocean replacement times based on Th supply, averaged for the whole North Atlantic Basin in this study versus the residence times estimated by Li (1991) based on removal by sedimentation. The y axis error bars reflect uncertainty in the REE/Th composition of source material and the relative solubility ratio. The dotted line is the 1-to-1 line. REE = rare earth element.

data available at the time, they are generally consistent with the lower end of the ranges we calculate using the Th technique specific to the North Atlantic. More importantly, the trend in residence/replacement time is consistent (Table 1 and Figure 4). This also supports the notion that our replacement time estimates are somewhat overestimated due to lateral REE supply by AABW. Nonetheless, given the consistency in trend with atomic number and the absolute magnitude of the residence times, it appears that the Th-supply-based replacement times are relatively well constrained.

3.3. Prior Residence Time Estimates of the Bioactive Trace Elements

In addition to REE, the Th flux-based replacement time approach can be used to estimate the replacement times of bioactive trace elements of interest to marine biogeochemical processes: Mn, Fe, Co, Cu, Zn, and Cd. We also consider dissolved Al residence times in GA03, since Al is often used as the abiotic analog to the bioactive trace elements. All these elements are measured by GEOTRACES endeavors and are becoming the focus of biogeochemical modeling studies. While the geochemical cycles of these elements involve many biological transformations in which Th does not participate, their main source to the ocean is ultimately from the UCC, whether from dust, rivers, groundwater, or margin sediments, excluding hydrothermal inputs. Knowing this, we can proceed to estimate

the replacement times of these elements in the same way as for REEs, while highlighting the extent to which this approach is limited. For instance, hydrothermal inputs of these elements will lead the replacement time based on Th supply to overestimate the residence time (since hydrothermal vents supply little Th to the ocean, Pavia et al., 2018). Additionally, as in the case of the REEs, the contribution of preformed elements in AABW may also result in our approach overestimating residence time.

Before discussing our new replacement time estimates, it makes sense to review the best existing estimates of the ocean residence times of these elements (Table 2). There has been much progress in understanding the magnitudes of various trace element sources and sinks. Current best-estimate residence times for Zn, Cu, and Cd are 8,000–11,000 years (Little et al., 2016), 2,000–3,300 years (Little et al., 2017), and 26,000–55,000 years (Little et al., 2015), respectively, based on full oceanic mass balance calculations. These estimates are based on global sources and sinks, so we emphasize care taken in their comparison to the replacement times derived here, which are specific to the North Atlantic and do not necessarily include all relevant source fluxes. Bruland et al. (1994), deriving a residence time based on removal by sinking particles in the North Pacific, estimated a slightly shorter Zn residence time than the global residence time of Little et al. (2016) of 3,000–6,000 years. The Bruland et al. (1994) method produced a similar residence time estimate as Little et al. (2015) for Cd of 22,000–45,000 years. Finally, Roshan et al. (2016) also calculated a shorter Zn residence time ($3,000 \pm 600$ years) than Little et al. (2016), by adding recently observed hydrothermal sources of Zn to the sum of Zn sources compiled by Little et al. In contrast to these relatively long time scales, for Mn, Co, and Al, the best available estimates are much shorter than the time scale of deep ocean circulation (20–40 years [Bruland et al., 1994], 40–130 years [Hawco et al., 2017; Saito & Moffett, 2002], and 45–90 years [Bruland et al., 1994], respectively). These estimates are based on scavenging and particle sedimentation, likely the major removal mechanism for these elements. A recent global biogeochemical model of Co constrained with available GEOTRACES data estimated a global ocean Co residence time of 70 years (7 years in the upper 250 m and 250 years below 250 m, Tagliabue et al., 2018).

Constraining the residence time of Fe is an obvious community priority because of Fe's influential role as a key micronutrient in biogeochemical cycles and its consequent role in limiting primary productivity over large regions of the ocean. Thus, understanding how quickly the supply of Fe changes with time is of great significance to the global carbon cycle. Despite this importance, the propensity for Fe to be contaminated during collection and analysis has historically led to challenges in ascertaining Fe concentrations accurately. However, after accruing a larger data set of uncontaminated Fe analyses, two groups initially developed deep ocean Fe residence time estimates based on the scavenging rates of Fe in deep waters (70–140 years in the deep Pacific [Bruland et al., 1994] and 130–410 years in the deep Atlantic [Bergquist & Boyle, 2006]).

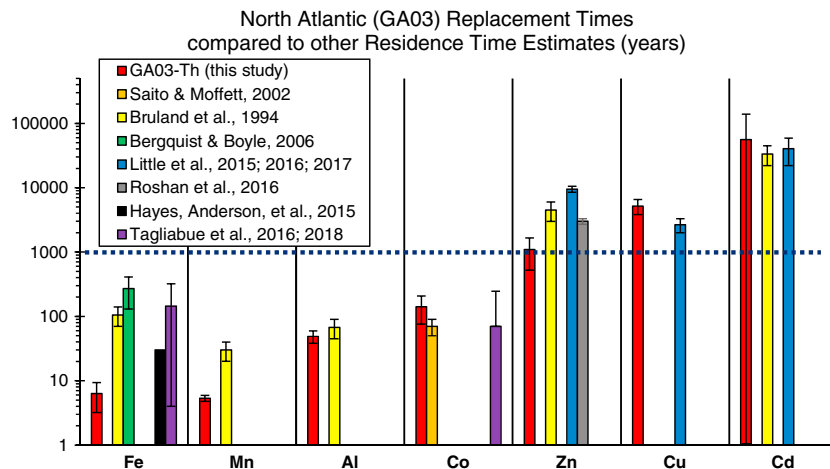


Figure 5. Replacement times for the bioactive elements from this study (whole North Atlantic average) compared with the best available residence time estimates from previous studies. The error bars on the GA03 data represent uncertainty associated with crustal composition and solubility. The dotted line at 1,000 years represents roughly the division of elements whose residence time is longer (Zn, Cu, and Cd) or shorter (Fe, Mn, Al, and Co) than the mixing time of the ocean.

More recently, Hayes, Fitzsimmons, et al. (2015) used the Th supply-based approach described in this study to estimate a deep Pacific Fe residence time near Hawaii of about 30 years. Because of the disagreement with the century-scale residence time estimates, those authors hypothesized that Th supply could somehow be decoupled from Fe supply in the deep ocean, resulting in a significant overestimation of the Fe supply and a residence time estimate that is too low. Recent results from modeling studies, however, are providing some support for the notion that the residence time of Fe may be decadal rather than centennial or could vary significantly between basins with different Fe speciation. In the intercomparison of global ocean iron models, 5 of the 13 models recently examined in a review by Tagliabue et al. (2016) gave global Fe residence times of less than 10 years, and 8 gave less than 50 years (average and standard deviation: 145 ± 176 years). Furthermore, Kipp et al. (2017) estimated a residence time of dissolved Fe in the hydrothermal plume emanating from the East Pacific Rise at 2.4-km depth of 9–20 years, based on scavenging rates of Fe in the plume. Thus, while each of these residence time estimates differs somewhat in their approach to defining a residence time, it is clear that there remains significant uncertainty in the residence time of Fe in the ocean.

The replacement times we derive here are specific to the North Atlantic, omit key sources such as hydrothermal vents and rivers, and are not necessarily representative of a steady state situation. Our comparison of replacement times to globally or regionally defined residence times in the literature is thus not meant to be strictly quantitative.

3.4. Replacement Times of the Bioactive Trace Elements Estimated With the Th-Based Approach

Here we estimate replacement times for the bioactive elements using the Th-based approach on the GA03 data set, with results shown for Fe, Mn, Al, Co, Zn, Cu, and Cd in Figures 5 and 6 and Table 2. The overall range in replacement times of the bioactive elements estimated here for the whole North Atlantic is for the most part consistent with the range of previous residence time estimates (Figure 5). North Atlantic Zn, Cd, and Cu replacement times are close to or longer than the ocean mixing time ($>1,000$ years), while those of Fe, Mn, Co, and Al are significantly shorter, decadal, or less. Figure 6 shows section views of the replacement time estimates using UCC composition and HAc leach solubility ratios, and Figure 7 shows the area-weighted average depth profile of the North Atlantic replacement times. The errors reported in Figures 5, 7 and Table 2 take into account uncertainty in the composition and solubility ratios by comparison with results of the calculation using North African dust and DI leach information. Uncertainty related to AABW supply or other *missing* terms in the steady state budget is not accounted for.

3.5. Upper Water Column Replacement Times of the Bioactive Trace Elements

While the focus of this manuscript is the North Atlantic basin-scale replacement times, the Th-supply method can be used at any integration depth and may indeed be quite useful in interpreting bioactive

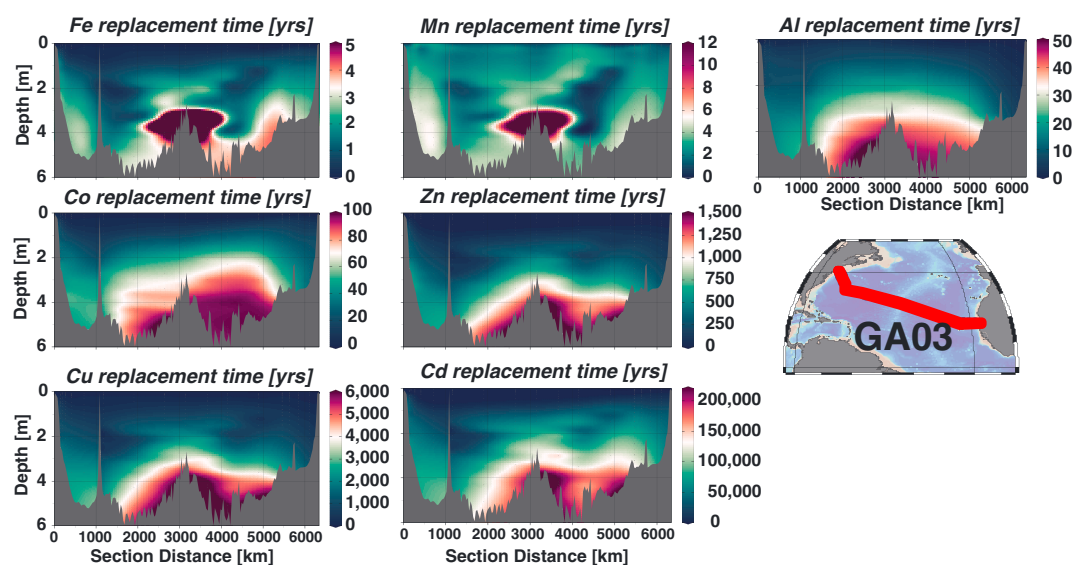


Figure 6. Replacement times of dissolved Fe, Zn, Mn, Cd, Cu, Co, and Al with respect to supply based on dissolved ^{232}Th input, assumed composition of the upper continental crust (Rudnick & Gao, 2014) and solubility ratios defined by mild acetic acid leaches of GA03 North African aerosols. The range in deep ocean (4 km) residence time estimates for these elements reported in Table 2 reflects uncertainty in source composition and solubility.

trace element behavior in the euphotic zone, as shown in the shallow portions of the section plots in Figure 7. These estimates, expanded for more detail in the upper 1 km, are presented with limited discussion in the supporting information for Fe, Mn, Al, Cu, Zn, Cd, and Co. In the upper water column, especially for elements with short residence times, rivers and preformed elements are much less likely to be significant contributors to the measured inventories. Therefore, in the upper ocean the Th-based approach may give a more reliable estimate of element replacement time specifically by dissolution of dust, as has been argued for Fe (Hayes, Fitzsimmons, et al., 2015). On the other hand, in considering the upper ocean alone, another potential source of elements may need to be considered, which is the upwelling of water with Z/Th ratios distinct from dust. A significant upwelling source may be limited to upwelling regions such as the Mauritanian margin, and thus basin-wide averaging is likely to reduce the bias introduced.

Lastly, with available GEOTRACES data, we can make both upper ocean and deep ocean replacement time estimates for Sc, V, Ni, Ga, and Ba. These estimates are also given in the supporting information.

4. Discussion

Our North Atlantic Fe replacement time of 6 ± 3 years is more similar to previous decadal or shorter estimates of residence time (Hayes, Fitzsimmons, et al., 2015; Kipp et al., 2017; Tagliabue et al., 2016) than the century-scale estimates (Bergquist & Boyle, 2006; Bruland et al., 1994). In making these comparisons, it is worth noting that our Th-based Fe replacement time could underestimate the residence time if the true value of $S_{\text{Fe}}/S_{\text{Th}}$ is less than ~ 0.5 – 1.3 . However, the true $S_{\text{Fe}}/S_{\text{Th}}$ value would have to be less than 0.05 to produce a century-length dissolved Fe replacement time. Of course, different regions of the ocean are likely to be characterized by different effective relative solubility ratios because of different chemical conditions or distinct sources (Figure 1). For instance, Fe could be much more effectively leached from dust than Th in surface waters due to biological activity, photoactivity, easily weathered surface oxide coatings, and/or ligand influences. In contrast, in abyssal waters, Th could continue to be leached where there is less Fe released (thus, $S_{\text{Fe}}/S_{\text{Th}}$ could be higher in surface waters and lower in deep waters). Different organic ligands and ambient conditions could also play a role. Such water column variability is not considered in our calculation here; however, the relative solubility number represents the integrated dissolution of both elements throughout the water column, whatever the depth profile of relative solubility might look like. The true integrated $S_{\text{Fe}}/S_{\text{Th}}$ would thus again need to be quite low to produce a centennial replacement time in this case.

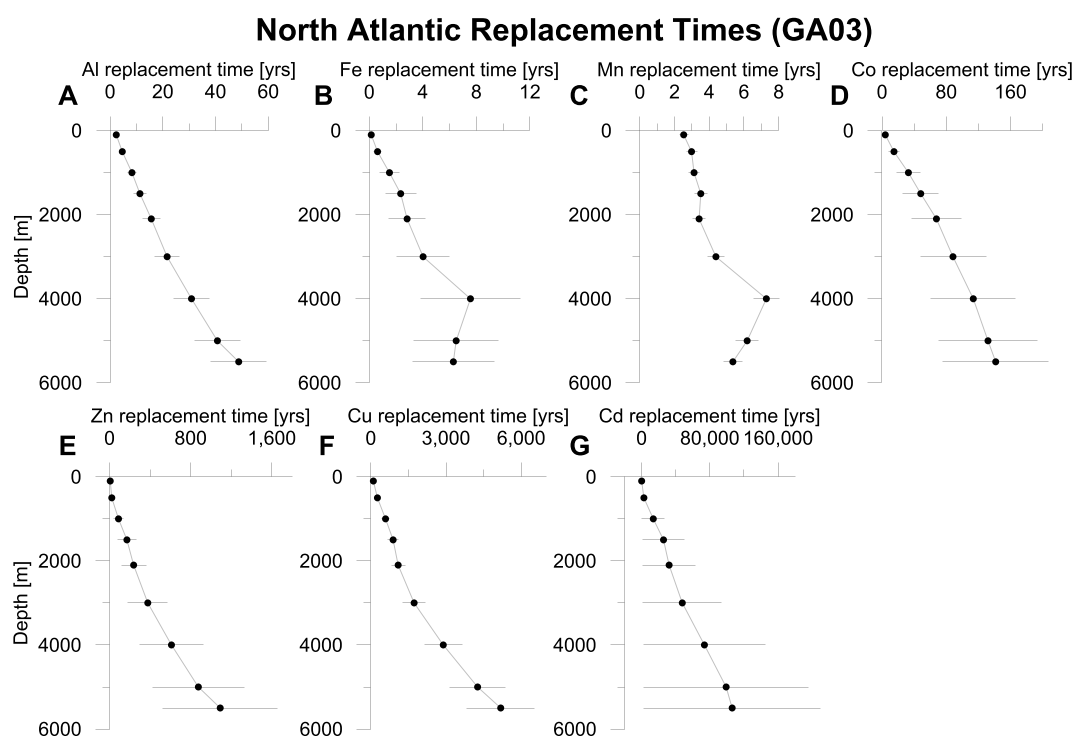


Figure 7. Trace element replacement times with respect to supply based on ^{232}Th supply. These profiles represent replacement times as a function of integration depth. To make a basin-wide average, the GA03 station profiles were averaged in depth bins on an area-weighted basis. The error bars represent the uncertainty in values used for the composition of the source (UCC or Saharan dust) and the relative solubility ratio (DI leach or HAC leach). For Mn, Zn, and Cu, the solubility ratio defined by the HAC leach was used as the relative solubility from the DI leach for these elements were highly uncertain (see Table 2). Note that the Cd error bars nearly overlap with zero. HAC = acetic acid; UCC = upper continental crust; DI = deionized water.

The very short North Atlantic replacement time for Mn (5 ± 1 years) implies rapid removal by processes such as biological uptake, oxidation, and/or particle scavenging. Nonetheless, if the true $S_{\text{Mn}}/S_{\text{Th}}$ value were less than ~ 10 as used here, our replacement time estimates would increase, perhaps to be more in line with the previous residence time estimate of 20–40 years (Table 2). It might be that in leaching experiments, relative Mn/Th solubility is greater than what would occur in situ in the ocean. Further investigation into how relative solubility ratios change in different leaching methods may shed light on this issue.

The North Atlantic replacement time for Co in this analysis (140 ± 70 years) is similar to the best previous residence time estimates (Hawco et al., 2017; Saito & Moffett, 2002; Tagliabue et al., 2018). Additionally, Al has a deep ocean replacement time of 50 ± 10 years, again broadly consistent with previous residence time estimates (Bruland et al., 1994; Chester & Jickells, 2012) and being slightly longer than the residence time of Th, also expected based on previous work (e.g., Moran & Moore, 1989). The mid-ocean ridge in the vicinity of GA03 may be a source of Al, either from hydrothermal input (Measures et al., 2015) or sediment dissolution on the flanks of the ridge (Middag et al., 2015), and either source would contribute to our replacement time overestimating the true residence time here.

The hydrothermal plume at the GA03 Mid-Atlantic Ridge is clearly a large source of Fe and Mn (Conway & John, 2014a; Hatta et al., 2015) that would not be accounted for by Th-based estimates of Fe and Mn supply. The Th-based dissolved Fe flux at the depth of the hydrothermal plume in GA03 is about $640 \mu\text{mol}/\text{m}^2/\text{year}$. The Th-based dissolved Fe replacement time rises to 30 years in the plume, compared to 5 years at the same depth in surrounding stations (Figure 6). In the basin-averaged data (Figure 7), the full magnitude of this anomaly is partly averaged out, but an increase at the depth of the ridge crest ($\sim 3,500$ m) is still apparent. If the overall Fe residence time should be 5 (rather than 30) years in the deep North Atlantic, then the Fe flux at the ridge site would have to be 6 times larger than the Th-based estimate, implying about $3,200 \mu\text{mol}/\text{m}^2/\text{year}$.

year of hydrothermal Fe being added (see equation (4)). This is much higher than our current best estimates of the hydrothermal Fe flux, $100 \mu\text{mol}/\text{m}^2/\text{year}$ in the Atlantic and $300 \mu\text{mol}/\text{m}^2/\text{year}$ in the Pacific (Tagliabue et al., 2010). In one sense, this finding offers support for the idea that the hydrothermal Fe flux from the Atlantic mid-ocean ridge is higher than would be expected based on its relatively slow spreading rate (Saito et al., 2013). On the other hand, the observation that dissolved Fe is transported in the deep ocean 4,000 km away from a large source in the East Pacific Rise (Fitzsimmons et al., 2014; Resing et al., 2015) suggests that the hydrothermal Fe must remain in the deep ocean longer than a few years. However, this behavior may be ridge specific or even vent specific, depending on ambient conditions and vent chemistry, such as the presence of H_2S .

One explanation for the persistence of Fe in deep water in the Pacific invokes stabilization by colloids and/or ligands (Fitzsimmons et al., 2016, 2017) that may also have an origin in the hydrothermal plumes and that may not apply to lithogenic Fe from other sources. Thus, if Fe speciation or organic ligands are contributing to an apparently longer residence time in the plume measured in the GA03 section, then the estimated hydrothermal Fe flux would not be as drastically high as calculated above. When Th and Fe data from the GEOTRACES program become available for other mid-ocean ridges in the Pacific, Arctic, and Indian Oceans, we may gain more insight into how apparent anomalies in Th-supply-based Fe replacement times can be used to constrain hydrothermal Fe fluxes.

Similarly, the Th-based dissolved Mn flux is roughly $125 \mu\text{mol}/\text{m}^2/\text{year}$ at the deep ridge site, while the Th-based replacement time there is 40 years (Figure 6) rather than the 5 year replacement time of the basin-wide average (Figure 7), implying a factor of 8 increased Mn flux (an additional $875 \mu\text{mol}/\text{m}^2/\text{year}$ Mn flux from hydrothermal sources) to bring the replacement time estimate in line with the deep ocean average. Current estimates put the hydrothermal Mn flux at $10\text{--}20 \mu\text{mol}/\text{m}^2/\text{year}$ along the ridge (van Hulten et al., 2017). Thus, either the Th-based replacement times imply a much higher hydrothermal Mn flux than is currently assumed or again perhaps the residence time of Mn increases in the deep ocean near ridges due to stabilizing ligands of hydrothermal origin (Sander & Koschinsky, 2011), similar to Fe.

The millennial-scale replacement time of dissolved Zn estimated here ($1,100 \pm 600$ years) is short compared to the most recent residence estimates 3,000–11,000 years (Bruland et al., 1994; Little et al., 2016; Roshan et al., 2016), but at least similar in order of magnitude, given the uncertainties involved. Additionally, Zn concentrations increase in the deep ocean along the conveyor circulation from the North Atlantic to the North Pacific by about a factor of 5 (Bruland et al., 2014). Thus, if calculated with a given Zn supply, one would expect a replacement time estimate to increase from the North Atlantic to the North Pacific or global ocean. Interestingly, the mid-ocean ridge does not appear to be a great source of Zn in the Atlantic (Roshan & Wu, 2015a), but it does in the Pacific and has been hypothesized to be an important global source (Roshan et al., 2016). This Zn source would clearly not be accounted for by Th supply, but this would mean our ~1,000-year replacement time estimate would overestimate the residence time due to not including a hydrothermal flux.

The other bioactive elements largely supplied by rivers, Cd and Cu, yielded replacement time estimates similar to previous estimates (Table 2, Bruland et al., 1994; Little et al., 2015, 2017), though the estimates here have large uncertainties related to composition and solubility assumptions. For instance, using UCC composition and HAc leach solubility, the deep ocean replacement time of dissolved Cd averages 180,000 years (Figure 6), but if we use North African dust composition and DI leach solubility, this estimate drops by 2 orders of magnitude to 1,800 years. As mentioned above, because the North African dust end-member may be contaminated by anthropogenic Cd, we take the average of the two possible estimates using the UCC composition (with DI leach and HAc leach) for the average North Atlantic Cd replacement time (180,000 and 33,000 years, average and standard deviation being $106,000 \pm 103,000$ years). This large uncertainty highlights the difficulty presented by predicting the replacement time of a mostly river supplied element like Cd with a mostly dust supplied element like Th.

In the case of Cu, uncertainty in both composition and solubility ratio leads to a fairly large range in replacement time estimates ($5,200 \pm 1,400$ years) with little reason to discount any of the parameters used. The geographical structure of the replacement time estimates (Figure 6) of Zn, Cd, and Cu is similar to those of the REEs, yielding increasing replacement times in the deep eastern Atlantic basin. It is likely that all of these elements have some supply from AABW into the North Atlantic (Conway & John, 2014b, 2015; Jacquot & Moffett,

2015; Roshan & Wu, 2015a, 2015b; Wu & Roshan, 2015). While the assumption of Th supply being a good analog for the supply of other elements may be appropriate for some elements, it seems most tenuous for Zn, Cd, and Cu. Nonetheless, our results at least agree with previous assessments that these elements have residence times similar to or longer than the timescale of ocean mixing (~1,000 years).

5. Conclusion

Extrapolating the Th cycle to other elements in the periodic table has proved useful in assessing the range of trace element reactivity exhibited along the GA03 section in the North Atlantic and has potential applicability to the global ocean. Proof of concept for this method is demonstrated from Th-based replacement times of the REEs that follow known patterns of scavenging intensity. Among the bioactive elements, the evidence presented here suggests that the dissolved Fe residence time in the North Atlantic is decadal rather than centennial, and Fe and Mn may have the shortest residence times of all the elements in the ocean. Our Th-derived replacement time estimates for Zn, Cd, Cu, Co, and Al largely agree with the best available estimates. Chief among the uncertainties associated with Th-based replacement times for the bioactive elements is how to define an appropriate source composition. Alternatively, if input ratios of specific sources (e.g., groundwater, modified estuarine water, or anthropogenically contaminated water) could be better defined, a more complete assessment of trace element sources can be defined. The relatively simple Th-based replacement time method presented here can inform biogeochemical modeling of all trace elements and may be particularly useful for constraining the extremely rapidly cycled bioactive elements, Fe and Mn.

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